High strength aluminum alloy resistant to exfoliation and method of heat treatment

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Abstract of **GB2114601**

The method comprises providing an aluminum-base alloy comprising 5.9 to 8.2 wt.% zinc, 1.5 to 40 wt.% magnesium, 1.5 to 3.0 wt.% copper and 0.5 wt.% maximum other alloying elements such as zirconium, chromium, manganese, iron, silicon and titanium, with the balance consisting of aluminum, working the alloy into a product of predetermined shape, solution heat treating the shaped product, quenching, and aging the heat treated and quenched product at a temperature of from about 270 DEG F. to 285 DEG F. for a period of from 6 to 30 hours.

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(54) High strength aluminum alloy resistant to exfoliation and method of heat treatment

(57) The method comprises providing an aluminum-base alloy comprising 5.9 to 8.2 wt.% zinc, 1.5 to 4.0 wt.% magnesium, 1.5 to 3.0 wt.% copper and 0.5 wt.% maximum other alloying elements such as zirconium, chromium, manganese, iron, silicon and titanium, with the balance consisting of aluminum, working the alloy into a product of predetermined shape, solution heat treating the shaped product, quenching, and aging the heat treated and quenched product at a temperature of from about 270°F. to 285°F. for a period of from 6 to 30 hours.

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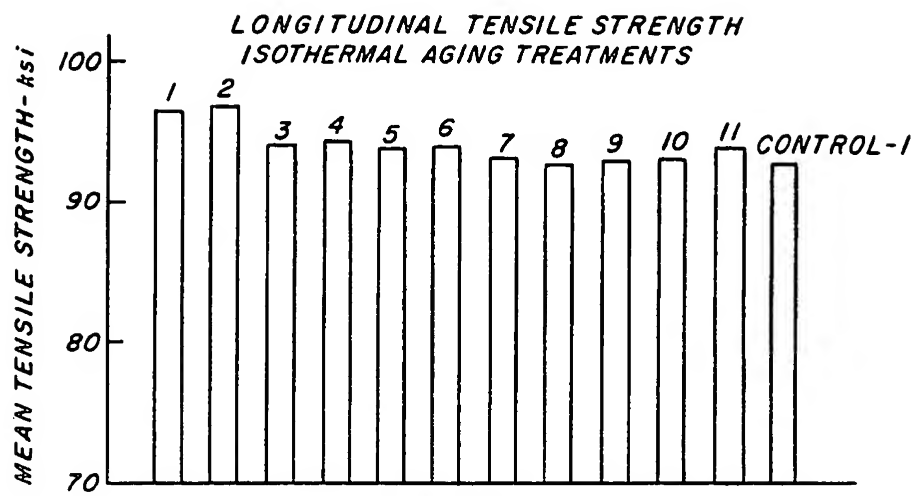


FIG. 1.

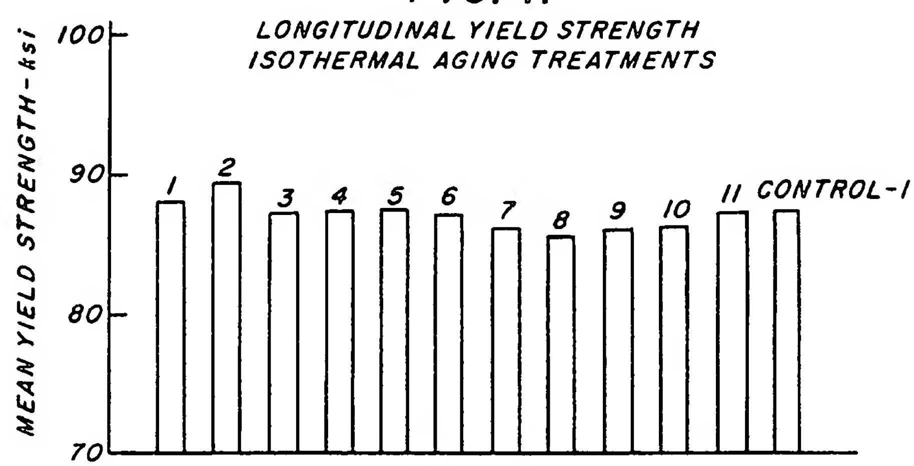


FIG. 2.

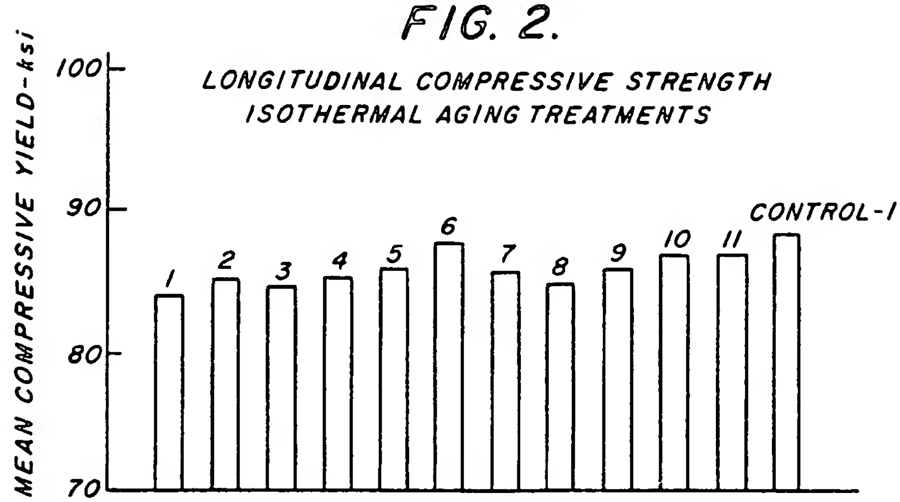


FIG. 3.

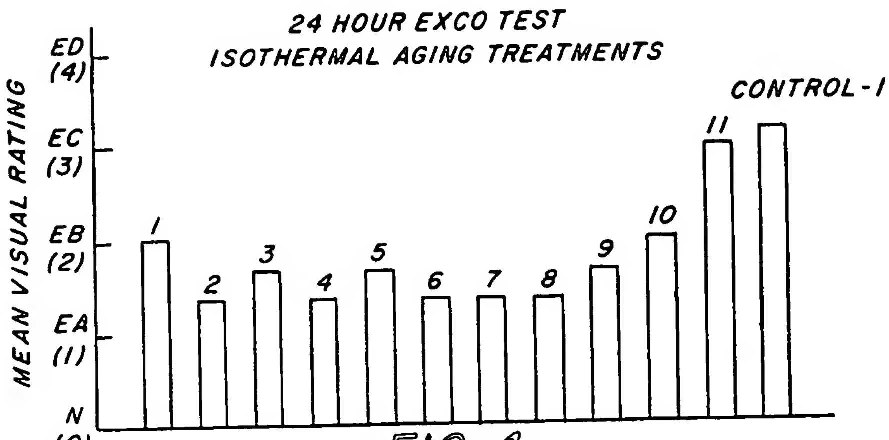


FIG. 4.

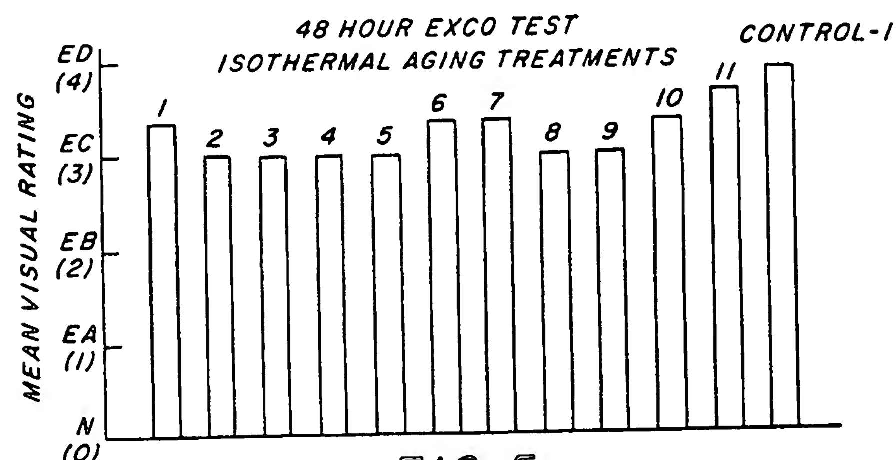


FIG. 5.

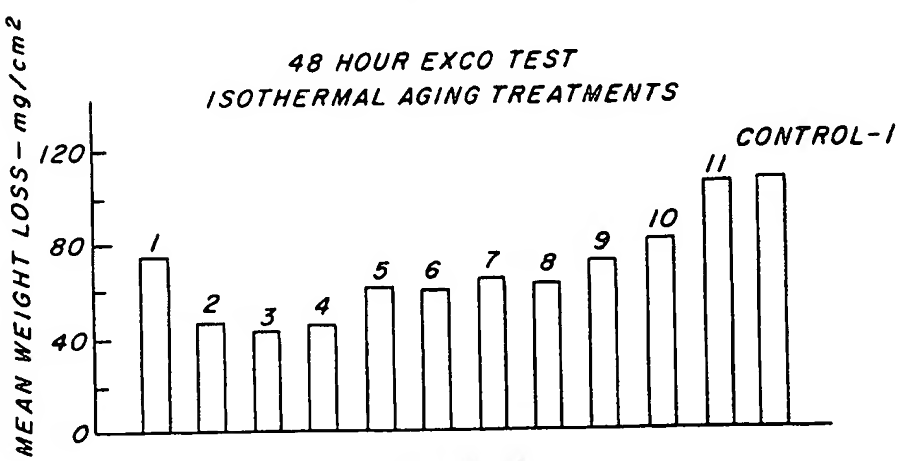
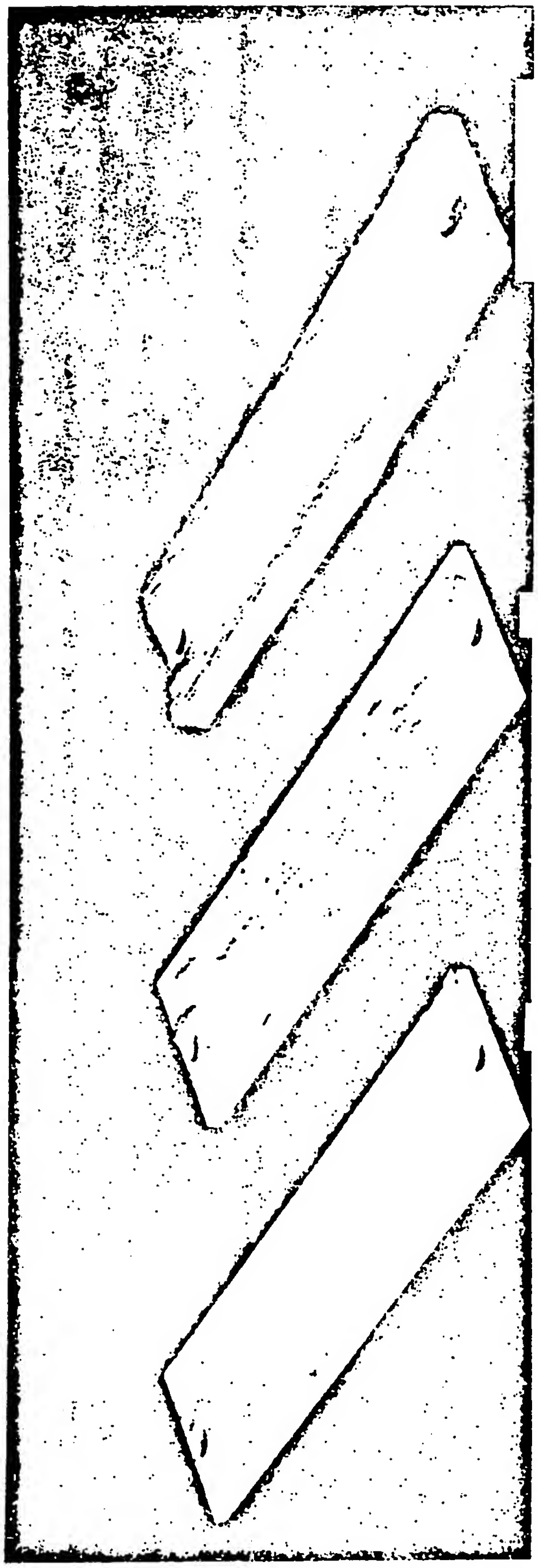


FIG. 6.

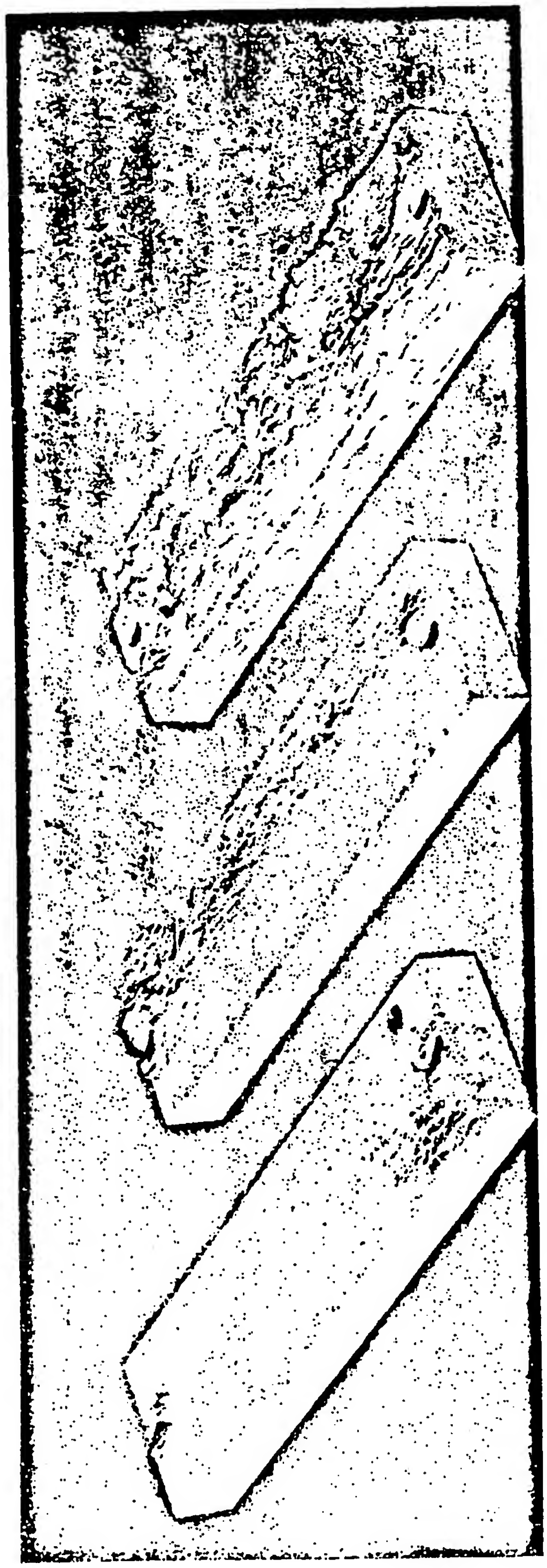


CONTROL

16 HOURS AT 275° F.

12 HOURS AT 275° F.

FIG. 7.



CONTROL

16 HOURS AT 275° F.

12 HOURS AT 275° F.

FIG. 8.

SPECIFICATION

High strength aluminum alloy resistant to exfoliation and method of making

Aluminum alloys in the 7000 series containing high amounts of zinc, copper and magnesium are known for their high strength-to-weight ratios and, therefore, find application in the aircraft industry. Such applications, however, result in exposure to a wide variety of climatic conditions necessitating careful control of working and aging conditions to provide adequate strength and resistance to corrosion, including both stress corrosion and exfoliation.

Conventional alloys of this type such as 7075, which contain 3 to 8 wt.% Zn, 1.5 to 5 wt.% Mg and 0.75 to 2.5 wt.% Cu, can be aged at a temperature of about 215°F. to 250°F. to obtain excellent strength properties in what is known as the T6 temper. High resistance to exfoliation and stress corrosion with some sacrifice in strength can be achieved by subsequently aging the alloy at temperatures of 300°F. to 350°F. for a sufficient period of time to achieve what is known as a T7 temper.

In some instances, modifications of the above tempers have been successfully made by careful control of the amounts of alloying materials combined with the use of elevated temperatures. For example, Staley et al, U.S. Patent 3,881,966, disclose and claim a method for obtaining a 7000 series alloy exhibiting high strength and high resistance to stress corrosion utilizing an aging temperature of 300°F. to 380°F. in combination with careful control of the ratio of alloying constituents.

Aging at lower temperatures to achieve the same results has also been accomplished using other alloying constituents. For example, Markworth et al, U.S. Patent 3,794,531, teaches the use of single stage aging at a temperature of 212°F. to 284°F. by substituting 2% of the zinc content with cadmium.

The use of nickel as an additive in 7000 series alloys to achieve resistance to stress corrosion is taught by Zeigler et al in U.S. Patent 2,403,037. This alloy is said to be aged in a single step at temperatures of 275°F. to 350°F.

While the use of a single step aging process has advantages from the standpoint of efficiency and energy conservation, the continuing search for alloys with higher strength properties compounds the problem of maintaining the desired resistance to stress corrosion as well as resistance to exfoliation.

Thus, the prior art seems to indicate that such properties can be maintained using aging temperatures of over 300°F. with or without a prior aging step at lower temperatures. It was, therefore, quite surprising and disconcerting to find that the use of such aging (i.e. over 300°F.) on high strength alloy similar to that disclosed in the aforementioned Staley et al patent (U.S. Patent 3,881,966) resulted in lowered resistance to exfoliation if aging at temperatures of over 300°F. was carried out over a short period of time (less than 7 hours at 325°F., for example) and a loss in tensile strength if the aging period was extended.

Quite unexpectedly, it was discovered that the desired properties could be achieved in this alloy by lowering the aging temperature rather than raising the temperature as taught in the prior art.

Thus, in accordance with the preferred embodiment of the invention, an aluminum-base alloy having T6 strength properties and improved resistance to exfoliation is provided having, as alloying constituents and impurities: 5.9 to 8.2 wt.% zinc, 1.5 to 3.0 wt.% copper, 1.5 to 4.0 wt.% magnesium, 0.08 to 0.15 wt.% zirconium, 0.5 to 0.10 wt.% manganese, 0 to 0.04 wt.% chromium, 0 to 0.06 wt.% titanium, 0 to 0.12 wt.% silicon and 0 to 0.15 wt.% iron, not more then 0.05 wt.% of individual unidentified impurities and not more than 0.15 wt.% total unidentified impurities with the balance consisting of aluminum. The alloy product is subjected to hot working, solution heat treating and quenching followed by an aging process which consists of maintaining the alloy at a temperature of from above 270°F. to 285°F. for a period of from 6 to 30 hours.

In the accompanying drawings:

Figure 1 is a bar graph illustrating the longitudinal tensile strength achieved using various aging conditions.

Figure 2 is a bar graph illustrating the longitudinal yield strength achieved using various aging conditions.

Figure 3 is a bar graph illustrating the longitudinal compressive yield strength achieved using various aging conditions.

Figure 4 is a bar graph illustrating the resistance to exfoliation achieved after a 24-hour EXCO Test using various aging conditions.

Figure 5 is a bar graph illustrating the resistance to exfoliation after a 48-hour EXCO Test using various aging conditions.

Figure 6 is a bar graph illustrating the weight loss after a 48-hour EXCO Test using various aging conditions.

Figure 7 is an photograph illustrating 1-year exposure of 0.156 inch samples prepared in accordance with the invention as well as a control.

Figure 8 is a photograph illustrating 1-year exposure of 0.80 inch samples prepared in accordance with the invention as well as a control.

In accordance with the invention, an improved high strength 7000 series alumium alloy is provided having specific controlled amounts of alloying constituents and isothermally aged in a single step process.

The alloy of the invention contains the following ingredients: 5.9 to 8.2 wt.% zinc, preferably 5.9 to 6.9 wt.%; 1.5 to 4.0 wt.% magnesium, preferably 2.0 to 2.7 wt.%; 1.5 to 3.0 wt.% copper, preferably 1.9 to 2.5 wt.%; 0.05 to 0.25 wt.% zirconium, preferably 0.08 to 0.15 wt.%; and not more than the following amounts of other alloying materials and impurities: 0.1 wt.% manganese, 0.04 wt.% chromium, 0.06 wt.% titanium, 0.12 wt.% silicon, 0.15 wt.% iron and 0.05 wt.% of individual unidentified impurities with a maximum total of 0.15 wt.% of unidentified impurities. The alloy develops improved resistance to exfoliation by aging at a temperature of from above 270°F. to 285°F. for a period of from 6 to 30 hours. That is, the improved resistance is characterized by significantly decreasing the rate at which exfoliation takes place, as will be seen by comparing the control and invention samples after exposure as shown in Figs. 7 and 8.

The alloy of the invention is useful in the production of extruded products, rolled materials such as sheet or plate, or in the form of forgings with the greatest benefit being obtained in extruded products, particularly with respect to 7150 tyoe alloy. It can be used in the form of thin products such as sheets as well as in heavier thicknesses such as plate without appreciable differences in yield strength due to differing quench rates.

The alloy of the invention having improved exfoliation resistance may be fabricated into various shapes and forms using conventional procedures as described in the aforementioned Staley et al patent (U.S. Patent 3,881,966). For example, the alloy composition may be provided as a continuously direct chilled cast ingot which is first subjected to an elevated temperature of about 850°F. to 900°F. for a period sufficient to homogenize its internal structure and uniformly distribute the alloying constituents therein. The material is then hot worked and, if desired, cold worked to produce the desired product. As previously discussed, these working conditions may include rolling, extruding or forging as well as any other known metal working procedures useful in fabricating aluminum structures. Intermediate annealing or reheating can also be employed if desired during the metal working steps if needed to produce the final desired product. The final product may be of relatively thick cross section, for example 2 to 4 inches or more in thickness, or it may be a relatively thin section of less than 1/4 inch. Regardless of thickness, the alloy product will exhibit a very satisfactory yield strength and improved resistance to exfoliation when aged in accordance with the invention and at little or no expense in stress corrosion resistance.

The product, e.g. plate, sheet or extrusion, is typically solution heat treated at a temperature of 860°F. or higher for a sufficient time for solution effects to approach equilibrium and then quenched. Quenching can be accomplished in a number of ways in view of the surprising lack of quench sensitivity possessed by the preferred alloys, e.g. 7150 type, useful in the invention. For example, the product can be quenched by spraying with cold water or immersed in room temperature water.

The heat treated and quenched product is then aged to develop its strength and improved resistance to exfoliation. The aging is carried out for a period of from 6 to 30 hours at a temperature of from above 270°F. to 285°F., preferably 271°F. to 280°F. and most preferably at 275°F. ± one degree. That is, aging is done in one step under isothermal conditions.

The following examples will serve to further illustrate the invention.

Example 1

Estrusions of 0.156, 0.250 and 0.80 inch were prepared and subjected to various aging times and temperatures, including a two-step aging process illustrative of the prior art wherein the sample is aged for up to 20 hours at a temperature of 250°F. or less followed by a second step at a temperature of 325°F. for about 5 hours. The alloy used contained (in parts by weight) 5.9 to 6.9 parts zinc, 2.0 to 2.7 parts magnesium, 1.9 to 2.5 parts copper, 0.1 part manganese, less than 0.04 part chromium, less than 0.08 to 0.15 part zirconium, less than 0.06 part titanium, less than 0.12 part silicon, less than 0.15 part iron and less than 0.15 part of unidentified impurities, with the balance aluminum. The extrusions were all solution heat treated at 890°F. to 900°F., cold water quenched and then stretched 1-1/2 to 2% prior to the aging step. After aging, the samples were measured for tensile and compression strength properties and then subjected to the EXCO Exfoliation Test defined in ASTM G34–79. The results are tabulated in Tables I, II and III, which differentiate between the three thicknesses of samples and in Figs. 1 through 6 in which the results for the three thicknesses have been averaged. The results clearly indicate that samples 3 through 6, which were aged in accordance

with the invention, regardless of thickness, maintain physical strength characteristics at least comparable to that achieved using the prior art of two-step aging process while providing marked improvement in exfoliation characteristics, as evidenced both by the visual ratings of the EXCO Test and by weight loss measurements.

TABLE I

MECHANICAL PROPERTY AND ACCELERATED EXFOLIATION TESTS, 0.156 IN THICK SAMPLES

Sample No.	Aging Treatment Time(hr)	Aging Treatment Temp. (°F)	Longitudinal Properties: Tensile T.S. ksi	Tensile Y.S (1) ksi	Tensile %El.	Compressive Yield Strength (1) ksi	24 Hr. EXCO Test ASTM Visual Rating (2)	48 Hr. EXCO Test ASTM Visual Rating (2)	48 Hr. EXCO Test Weight Loss mg/cm²
Control-1			92.1	86.2	10.2	87.2	E–D	E–D	110
Control-2			92.2	86.5	10.0	86.8	E–C	E–D	115
1	12	250	95.1	85.6	13.2	82.4	E–B	E–C	53
2	24	250	95.1	86.7	13.2	83.8	E–A	E–C	32
3	8	275	92.2	84.2	12.2	82.7	E–A	E–C	37
4	12	275	92.4	83.8	13.2	83.6	E–A	E–C	41
5	16	275	92.3	84.3	12.2	83.3	E–A	E–C	43
6	24	275	92.8	84.3	12.2	83.6	E–B	E–D	63
7	4	300	92.0	83.3	14.2	83.0	E–B	E–D	66
8	8	300	90.4	81.7	12.2	83.1	E–B	E–C	54
9	12	300	90.7	82.3	12.2	83.4	E–B	E–C	52
10	16	300	91.2	83.3	12.2	84.8	E–B	E–C	63
11	24	300	93.0	85.3	13.2	85.6	E–C	E–D	112

Notes: (1) Offset equal 0.2%
(2) Ratings based upon ASTM standards for exfoliation (Designation G–34–79) with A through D categories, D being most severe.

TABLE II
MECHANICAL PROPERTY AND ACCELERATED EXFOLIATION TESTS, 0.156 IN THICK SAMPLES

Sample No.	Aging Treatment Time(hr)	Aging Treatment Temp. (°F)	Longitudinal Properties: Tensile T.S. ksi	Tensile Y.S (1) ksi	Tensile %El.	Compressive Yield Strength (1) ksi	24 Hr. EXCO Test ASTM Visual Rating (2)	48 Hr. EXCO Test ASTM Visual Rating (2)	48 Hr. EXCO Test Weight Loss mg/cm²
Control–1			92.5	86.5	11.0	88.1	E–C	E–D	148
Control–2			93.7	88.1	12.2	88.9	E–C	E–D	127
1	12	250	94.1	86.2	13.2	82.8	E–B	E–D	100
2	24	250	95.4	87.4	14.2	82.8	E–A	E–B	52
3	8	275	92.9	85.3	12.2	82.6	E–B	E–C	58
4	12	275	92.6	85.4	13.3	82.0	E–A	E–B	44
5	16	275	92.0	85.0	11.2	84.3	E–A	E–C	59
6	24	275	93.7	86.6	14.2	85.3	E–B	E–C	50
7	4	300	90.5	83.5	13.2	86.2	E–B	E–C	55
8	8	300	91.0	83.5	14.2	83.0	E–B	E–C	67
9	12	300	91.0	83.1	13.2	84.5	E–B	E–C	75
10	16	300	91.7	84.3	14.2	86.4	E–B	E–D	102
11	24	300	92.2	85.5	15.2	85.7	E–C	E–D	126

Notes: (1) Offset equal 0.2%
(2) Ratings based upon ASTM standards for exfoliation (Designation G–34–79) with A through D categories, D being most severe.

TABLE III

MECHANICAL PROPERTY AND ACCELERATED EXFOLIATION TESTS, 0.156 IN THICK SAMPLES

			Longitudinal Properties				24 Hr. EXCO Test	48 Hr. EXCO Test	
	Aging Treatment		Tensile			Compressive Yield Strength (1)			
Sample No.	Time(hr)	Temp. (°F)	T.S. ksi	Y.S (1) ksi	%El.	ksi	ASTM Visual Rating (2)	ASTM Visual Rating (2)	Weight Loss mg/cm²
Control-1			93.9	88.6	11.5	88.7	E-C	E-C	63
Control-2			93.8	89.4	12.0	89.4	E-C	E-D	72
1	12	250	99.9	92.7	13.2	85.4	E-B	E-C	72
2	24	250	100.2	93.5	13.2	87.7	E-B	E-D	58
3	8	275	98.0	92.2	12.5	87.5	E-B	E-C	36
4	12	275	98.4	92.5	12.5	88.2	E-B	E-D	48
5	16	275	98.4	92.8	12.5	88.5	E-C	E-C	80
6	24	275	95.9	90.3	11.8	94.1	E-A	E-C	64
7	4	300	97.8	92.0	12.5	87.5	E-A	E-C	68
8	8	300	97.1	91.4	11.8	87.5	E-A	E-C	65
9	12	300	97.5	92.2	11.8	88.5	E-B	E-C	90
10	16	300	96.9	91.2	11.1	88.8	E-B	E-C	80
11	24	300	96.7	90.8	11.8	88.8	E-C	E-C	81

Notes: (1) Offset equal 0.2%

(2) Ratings based upon ASTM standards for exfoliation (Designation G-34-79) with A through D categories, D being most severe.

Example 2

To further illustrate the invention, samples prepared in accordance with Example 1 and aged for varying time periods of 8 to 24 hours at 275°F. in accordance with the invention were exposed for 12 months to a sea-coast atmosphere at Point Judith, Rhode Island. As in Example 1, control panels using the same alloy but using the conventional two-step aging process described in Example 1 were also exposed. As a further control, 0.250 inch and 0.8 inch thick samples of Alloy 7075–T 6511 were also exposed. This alloy, while not possessing the mechanical properties of the alloy used in the invention, is known to have good exfoliation resistance. The panels were exposed at a 45° angle with the test surface facing downward toward the earth since exfoliation corrosion is known to develop more quickly on sheltered surfaces. Visual examination of the panels after 12 months showed exfoliation attack on the prior art two-step aged panels of the degree E–C or E–D, whereas the panels aged in accordance with the invention showed milder exfoliation attack of the degree E–A or E–B.

Figures 7 and 8, respectively, illustrate the results of this 12 month exposure on the 0.156 inch and 0.80 inch samples. The samples shown in Fig. 7, are listed respectively in Table I as Sample No. 4, Sample No. 5 and Control-1. The samples in Fig. 8 conform resepctively to Sample No. 4, Sample No. 5 and Control-1 listed in Table III. The improved resistance to exfoliation is markedly evident from examination of Figs. 7 and 8.

Thus, the test results indicate that alloys composed of the recited constituents can be aged in a single step at a temperature of from above 270°F. to 285°F to produce a product having comparable mechanical properties and improved exfoliation resistance properties to that obtained using the two-step aging processes of the prior art.

CLAIMS

1. A method for producing a high strength aluminum alloy characterized by improved resistance to exfoliation which comprises:

(a) providing an aluminum-base alloy comprising 5.9 to 8.2 wt.% zinc, 1.5 to 4.0 wt.% magnesium, 1.5 to 3.0 wt.% copper and 0.5 wt.% maximum other alloying constituents and impurities with the balance consisting of aluminum;

(b) working the alloy into a product of predetermined shape;

(c) heat treating the shaped product;

(d) quenching and aging the heat treated product at a temperature of from about 270°F. to 285°F. for a period of from 6 to 30 hours.

2. The method of claim 1, wherein the aging is carried out at a temperature of from 271°F. to 280°F.

3. The method of claim 1, wherein the aging is carried out at a temperature of 275°F. plus or minus one degree.

4. The method of claim 2, wherein the product is heat treated at a temperature of about 850°F.

5. The method of claim 2, wherein said alloy contains not more than 0.04 wt.% chromium.

6. The method of claim 5, wherein said alloy contains 0.08 to 0.15 wt.% zirconium.

7. The method of claim 6, wherein said alloy contains not more than 0.06 wt.% titanium, 0.12 wt.% silicon, 0.15 wt.% iron as alloying constituents and 0.05 wt.% individual unidlentified impurities, the sum of said unidentified individual impurities not exceeding 0.15 wt.%

8. A method for producing high strength aluminum alloy characterized by improved resistance to exfoliation which comprises:

(a) providing an aluminum-base alloy containing, as alloying constituents, 5.9 to 8.2 wt.% zinc, 1.5 to 4.0 wt.% magnesium, 1.5 to 3.0 wt.% copper, 0.08 to 0.15 wt.% zirconium, 0.10 wt.% manganese; not more than the following maximum amounts of other alloying constituents: 0.04 wt.% chromium, 0.06 wt.% titanium, 0.12 wt.% silicon, 0.15 wt.% iron; and not more than 0.05 wt.% each of individual unidentified impurities with the balance consisting of aluminum;

(b) working said alloy to produce a product of desired shape;

(c) heat treating said product;

(d) quenching said product; and

(e) aging the product at a temperature of from above 270°F. to 285°F. for a period of from 6 to 60 hours.

9. An improved aluminum alloy having a compressive yield strength of at lest 77 ksi and improved resistance to exfoliation comprising an aluminum-base alloy containing, as alloying constituents, 5.9 to 6.9 wt.% zinc, 1.9 to 2.5 wt.% copper, 2.0 to 2.7 wt.% magnesium, 0.08 to 0.15 wt.% zirconium, 0.10 wt.% max. manganese, not more than 0.04 wt.% chromium, not more than 0.06 wt.% titanium, not more than 0.12 wt.% silicon, not more than 0.15 wt.% iron and not more than 0.05 wt.% of individual impurities and not more than 0.15 wt.% total other impurities, the balance consisting of aluminum, said alloy being initially hot worked to

achieve final desired form followed by solution heat treatment to place the solid constituents in solid solution, then quenched to retain the solid solution, and finally aged at a temperature of from above 270°F. to 285°F. for a period of 6 to 30 hours.

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